Process design using ionic liquids: Physical property modeling

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Abstract

Ionic liquids are a relatively new class of materials with properties that make them attractive for a wide variety of engineering applications. For design purposes, it is useful to have a relatively simple model (i.e., excess Gibbs energy model or equation-of-state model) capable of describing the physical properties and equilibrium behavior of ILs and IL solutions. We consider here the performance of two selected models, NRTL applied to the modeling of liquid-liquid equilibrium and an electrolyte equation-of-state applied to the modeling of aqueous mean ionic activity coefficients. In each case we focus on issues in parameter estimation, and use an approach based on interval mathematics to solve the parameter estimation problem globally. Sample results are presented and suggest that the models considered here may be useful for correlation of data, but may not be well suited for prediction.

Keywords: Ionic liquids, Parameter estimation, Phase equilibrium, Physical properties

1. Introduction

Room-temperature ionic liquids (ILs) are a relatively new class of materials that have attracted significant interest in the context of environmentally-conscious process design. These materials are salts but are liquids at room temperature. ILs have no measurable vapor pressure (i.e., they do not evaporate) and thus, from a safety and environmental viewpoint, have several potential advantages relative to the traditional volatile organic compounds (VOCs) used as solvents for reactions and separations, including elimination of hazards due to inhalation, explosion and air pollution. ILs also have many other interesting properties, including a wide liquidus range, that may make them attractive for a wide variety of engineering applications [1]. Thus, for engineering design purposes it is useful to have a relatively simple model (i.e., excess Gibbs energy model or equation-of-state model) capable of describing the physical properties and equilibrium behavior of ILs and IL solutions. As a basis for such models there is available today an increasing amount of physical property and phase equilibrium data [e.g., 2], as well as results from molecular simulation studies [e.g., 3].

The overall goal of this project is to evaluate the performance of a variety of models for computing the physical properties and phase behavior of ILs. Since the degree of dissociation in IL solutions is unclear, and there are molecular simulation results [4] that suggest that it may be small even in some dilute solutions, both electrolyte and nonelectrolyte models should be considered. In this abbreviated paper, we will present some initial results for two selected models. The first is the standard NRTL excess Gibbs energy model, without electrolyte extension, which will be applied to liquid-liquid equilibrium problems involving ILs. The second is the equation-of-state (EOS) model given by Myers et al. [5], which is an extension of the Peng-Robinson EOS to electrolyte systems, and which will be applied to aqueous IL solutions. It should be noted that, beyond standard EOS models, excess Gibbs energy models, and their electrolyte extensions, approaches such as QSPR [e.g., 6] and COSMO-RS [e.g., 7] also have potential in this context.

2. Methodology

2.1. Parameter Estimation

The models to be studied involve parameters that must be estimated from experimental data. Estimation of parameters in these models requires either the solution of a nonconvex global optimization problem, or the solution of a nonlinear equation system. Failure to find the globally optimal parameters for a thermodynamic model, and using locally optimal parameters instead, can have significant consequences in subsequent calculations, as demonstrated by Gau et al. [8] and Ulas et al. [9]. The use of locally optimal parameters can lead to rejection of a model that may perform satisfactorily when using globally optimal parameters. For example, Gau et al. [8] showed that using the globally optimal parameters improved the predictive capability of a model. In a problem involving the prediction of homogeneous azeotropes using the Wilson equation, they showed that using the locally optimal parameters given by Gmehling et al. [10] resulted in incorrect predictions of the number of azeotropes, but when using the globally optimal parameters the correct number of azeotropes was predicted. Therefore, in evaluating a model, it is important in doing parameter estimation that the method used will guarantee finding the globally optimal parameters. The interval-Newton approach provides such a methodology.

2.2. Interval-Newton Approach

For general background on interval mathematics, including interval-Newton methods, there are several good sources [e.g., 11]. The interval-Newton approach provides a method for computing *all* the solutions of a system of nonlinear equations, and doing so with *mathematical and computational certainty*. It can be applied directly to a parameter estimation problem formulated as an equation solving problem, or, for a problem formulated as an optimization problem, it can be applied to the equivalent system of equations (local optimality conditions). An important feature of this approach is that, unlike standard methods for nonlinear equation solving and/or optimization that require a *point* initialization, the interval-Newton approach requires only an initial *interval*, and this interval can be chosen to be sufficiently large to enclose all possible results of interest. Intervals are searched for solutions using a powerful root inclusion test based on interval mathematics. This test can determine with mathematical certainty if an interval contains no solution or if it contains a *unique* solution. If neither of these results can be proven, then typically the interval is bisected and the root inclusion test applied to each subinterval. On completion, an interval-Newton/generalized bisection (IN/GB) algorithm will have determined narrow enclosures of *all* the solutions to the equation system of interest. In an unconstrained optimization problem, these solutions represent the stationary points, including all local minima, so the global minimum can be readily determined. Alternatively, IN/GB can be applied in connection with a branch-and-bound scheme, which will lead directly to the global minimum without finding any of the other stationary points. In recent years, we have applied this technique to many problems in the modeling of phase behavior [e.g., 8,12].

3. Results

3.1. Modeling IL-Alcohol-Water Systems Using NRTL

One potential application of ILs is in the separation of fermentation broths. Thus, modeling the liquid-liquid equilibrium of IL-alcohol-water systems is of interest. The ternary system IL-octanol-water is also of particular interest since octanol-water partition coefficients are widely used as a measure of the potential ecological impact of a compound. The applicability of an excess Gibbs energy model (NRTL) to such systems is considered here. NRTL parameters for the underlying binary systems were determined using the procedure described below, and then these were used to predict the ternary behavior for comparison to experimental data.

When a binary system at constant temperature and pressure is modeled using a two-parameter excess Gibbs energy model, the parameters can be determined directly by using the equal activity condition for each component. This provides two equations:

$$\begin{aligned} &\ln \gamma_1^\alpha - \ln \gamma_1^\beta + \ln\left(\frac{x_1^\alpha}{x_1^\beta}\right) = 0 \\ &\ln \gamma_2^\alpha - \ln \gamma_2^\beta + \ln\left(\frac{1-x_1^\alpha}{1-x_1^\beta}\right) = 0 \ , \end{aligned} \tag{1}$$

where γ_i^π is the activity coefficient and x_i^π is the mole fraction of component i in phase π. The activity coefficients are functions of composition, involving two unknown parameters. Thus, by substituting the experimental values of x_i^π into Eq. (1), there remain only two unknowns, in this case the NRTL binary interaction parameters Δg_{12} and Δg_{21} (we will consider the NRTL nonrandomness factor to be fixed at $\alpha = 0.2$). For the NRTL model, it is well known [13] that there may be multiple solutions to this nonlinear equation system. Thus, it is important that we be able to determine *all* solutions. This is done using the IN/GB approach discussed above, which is guaranteed to find all solutions within a specified initial parameter interval, here chosen to be very large, namely $[-5\times10^6, 5\times10^6]$ J/mol for each parameter. Since Eq. (1) is a necessary but not sufficient condition for phase equilibrium, solutions must be tested to determine if they correspond to thermodynamically stable phase equilibrium. This can be done by using IN/GB to perform tangent plane analysis, as described by Tessier et al. [14], which guarantees that the phase stability problem is solved correctly. If multiple parameter solutions remain after testing for stability, then physical considerations must be used to choose the most appropriate values, since each solution represents an exact fit to the experimental data. For example, parameter values leading to the prediction of multiple miscibility gaps in the binary system can be eliminated, since this behavior is not observed experimentally. Or one can consider whether or not the sign and/or magnitude of the parameters are physically reasonable.

Using IN/GB in this framework, the NRTL parameters for alcohol-water, IL-water and IL-alcohol binaries were determined for a number of cases. Some sample results are shown in Tables 1 and 2 for the case in which the IL is 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and the alcohol is octanol. For the octanol-water binary, four parameter solutions to Eq. (1) were found. Solutions 1 and 2 predict stable states, but solution 2 shows two immiscibility gaps, so it is discarded. Solutions 3 and 4 predict unstable phases so they are discarded. Parameter solution 1 corresponds to the literature value [13] for this binary. For the [bmim][PF_6]-water binary, two solutions to Eq. (1) are found and both predict stable states.

However, solution 2 has a Δg_{12} value that is extremely large and can be considered physically unreasonable; therefore, it is discarded. The same procedure was used to determine the NRTL parameters from binary data at other temperatures of interest, and for other ILs and alcohols. A linear dependence of the parameters on temperature is observed. In general, NRTL can be used quite successfully to correlate the available binary LLE data involving ILs.

Table 1
NRTL parameters (J/mol) for *n*-octanol/water at T = 313K (Data from [13])

Solution No.	Δg_{12}	Δg_{21}	Stable?
1	99.52	22303.92	TRUE
2	58859.91	22356.01	TRUE
3	14293.37	120783.35	FALSE
4	12783.56	120877.45	FALSE

Table 2
NRTL parameters (J/mol) for [bmim][PF_6]/water at T = 298K (Data from [15])

Solution No.	Δg_{12}	Δg_{21}	Stable?
1	-556.43	16569.13	TRUE
2	-209974	21658.84	TRUE

Using parameter sets found from binary data as described above, the NRTL model was applied to predict IL/alcohol/water ternary diagrams. For the systems considered, the model predicts a three-phase region in IL/alcohol/water systems for alcohols with alkyl chains longer than ethanol. The three-phase region becomes smaller as temperature is increased and eventually disappears at a ternary upper critical solution temperature. In general, however, compared to experimental data [16] for such systems, NRTL does not show the right qualitative behavior, since a three-phase region has not been observed. From these results, it is reasonable to presume that, even though NRTL can successfully *correlate* binary data, it is not well suited to *predict* ternary phase diagrams from binary data. Therefore, we are investigating the use of the electrolyte NRTL model [17] as a tool for modeling these systems.

3.2. Modeling Aqueous Solutions with an Electrolyte Equation of State

In this section, we present some sample results for parameter estimation with the Myers et al. [5] EOS, applied to the modeling of mean ionic activity coefficients in aqueous solutions. This is a three parameter model. Two of the parameters are the van der Waals attraction parameter, *a*, and excluded volume parameter, *b*. The third parameter is σ, which is the hydrated radius of ions in solution. Myers et al. [5] have used experimental mean ionic activity coefficient data to estimate these parameters for a very large number of electrolytes in aqueous solution, and found that in general it correlates these data better than the (two-parameter) electrolyte NRTL model. However, the *a* values found span several orders of magnitude, and in general it is not clear that the parameter values reported are consistent with their physical interpretations. Previously [18], using local optimization methods, we have shown that the Myers et al. [5] EOS correlates activity coefficient data well for aqueous solutions of tetra-alkyl ammonium and choline salts, compounds whose structure is similar to that of some ILs. Again, the fit is somewhat better than that obtained [19] with electrolyte

NRTL, though again the parameter values span a wide range and have no clear physical meaning. This work also demonstrated that the least squares function arising in the parameter estimation for this EOS could have several local minima, and that thus global optimization methods really should be used.

Most existing data for mean ionic activity coefficients of aqueous electrolyte solutions was measured some time ago and does not include any volumetric data. However, more recent activity coefficient data, such as that currently being obtained for ILs, may also be complemented with density data as a function of composition. These two types of data can be combined to obtain data in the form of mean ionic activity coefficient $\gamma^{\pm}_{\mathrm{exp},i}$ as a function of solute density $\rho_i = x_i\rho = x_i/v$, where v indicates the molar volume of the solution and x_i the mole fraction of the solute. We show here some sample results for the model parameters a, b and σ when estimated from data in this form using the IN/GB methodology to globally minimize a simple least squares function. The problems used were designed to test the sensitivity of the optimal parameter values to small changes in the volumetric data used. The activity coefficient data used, along with five slightly different sets of volumetric data, are shown in Table 3. Thus, there are five sets of activity coefficient vs. solute density data for which parameter estimation can be done. These data sets should be regarded as hypothetical test problems.

Since this parameter estimation problem is an unconstrained optimization problem, the IN/GB approach can be applied to solve the first-order optimality condition for stationary points. It is assumed that the initial parameter interval is selected to be sufficiently large that it contains the global optimum in its interior. Since all stationary points in the initial parameter interval will be found, this also guarantees that the global minimum will be found. Table 4 shows the results of the parameter estimation for the data given in Table 3. It is observed that a wide range of σ values are obtained, varying by multiple orders of magnitude. Apparently, at least for these test problems, the optimal value of the σ parameter in the EOS is quite sensitive to small changes in the volumetric data used. This parameter represents the radius (given here in Å) of hydrated ions in solution and so the values found do not all appear to be physically meaningful. Our experience with these simple test problems, together with our previous experience [18], and the original results of Myers et al. [5], all suggest that optimal parameter values may vary over a wide range and often appear not to have physical significance. This is suggestive of a model that may correlate well, but not be well suited for prediction. We are currently investigating electrolyte extensions of other equation-of-state models for application to ILs and IL solutions.

4. Concluding Remarks

We have considered here the performance of two selected models, NRTL applied to the modeling of liquid-liquid equilibrium and an electrolyte equation-of-state applied to the modeling of aqueous mean ionic activity coefficients. An interval-Newton approach was used to ensure that parameter estimation problems were solved globally. The sample results presented suggest that the models considered here are useful for correlation of data involving ILs, but may not be well suited for prediction.

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Table 3
Data for EOS test problems: Molar volume and mean ionic activity coefficients versus solute molality *m*.

	Molar Volume (cm^3mol^{-1})				
case	$m = 0.1$	$m = 0.2$	$m = 0.3$	$m = 0.4$	$m = 0.5$
A	18.241	18.318	18.394	18.469	18.544
B	18.163	18.161	18.160	18.158	18.157
C	18.299	18.433	18.567	18.699	18.830
D	18.273	18.382	18.489	18.596	18.703
E	18.352	18.539	18.724	18.909	19.092
	Mean Ionic Activity Coefficients				
	0.7980	0.7520	0.7370	0.7280	0.7280

Table 4
Parameter estimation results for test problems using data in Table 3.

case	a ($Pa \cdot m^6mol^{-1}$)	b (cm^3mol^{-1})	σ (Å)
A	0.435	15.134	1244.8
B	0.763	16.194	7126.2
C	4.757	17.634	52.1
D	3.080	18.187	234.3
E	3.689	18.008	114.1

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